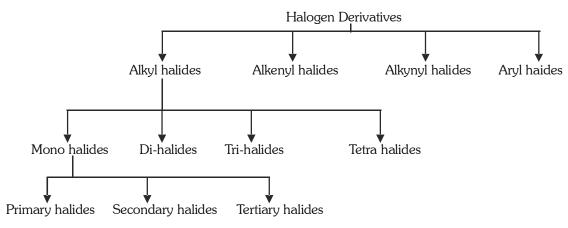
HALOGEN DERIVATIVES

1.0 HALOGEN DERIVATIVES

Compounds derived from hydrocarbons by replacement of one or more H-atoms by corresponding no. of halogen atoms are known as halogen derivatives.

2.0 CLASSIFICATION

On the basis of nature of hydrocarbon from which they are obtained, halogen derivatives can be classified as:



3.0 MONOHALIDES:

3.1 Genreal Methods of Preparation of Monohalides

(1) By direct halogenation of alkanes:

$$R-H + Cl_2 \xrightarrow{U.V.light} R-Cl + HCl$$
 (excess)

(2) By the addition of H-X on alkenes:

Isopropyl halide

- (3) By Alcohols:
 - (a) By the action of hydrogen halides:

$$R-CH_2-OH \xrightarrow{H-X} RCH_2-X$$

(b) By the action of phosphorous halides:

 PBr_3 and PI_3 are less stable, thus for bromides ($P + Br_2$) and for iodides ($P + I_2$) mixture is used.

(c) By reaction with thionyl chloride (Darzen's procedure):

Because of less stability of SOBr₂ and SOI₂, R—Br and RI can not be obtained by this method.



(4) Borodine - Hunsdicker's reaction:

R—COOAg +
$$X_2 \xrightarrow{CCl_4 \atop \Delta}$$
 R—X + CO_2 + AgX Silver salt of (Cl_2 or Br_2) a fatty acid

(5) By halide exchange:

R-Cl or R-Br + Kl
$$\xrightarrow{Acetone}$$
 R-I + KCl or KBr (Conant finkelstein reaction)
 $2CH_3Cl + Hg_2F_2 \xrightarrow{Water} 2CH_3-F + Hg_2Cl_2$ (Swart reaction)

Note : Finkelstein reaction can only be used to prepare R-I and swart's reaction can only be used to prepare R-F

3.2 Physical Properties

- (a) The lower members CH₃F, CH₃Cl, CH₃Br, C₂H₅Cl and C₂H₅F are gases at room temp.
- (b) Higher B.P. than parent alkanes.

Decreasing order of B.P. is :
$$R-I > R-Br > R-CI > R-F$$

among isomeric R—X, decreasing order of B.P. is : $Primary > Secondary > tertiary$

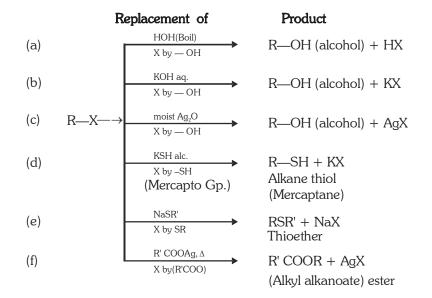
Decreasing order of density is : R-I > R-Br > R-CI > R-F

- (d) R-X are polar co-valent compounds but insoluble in water because they can not form H-bonds. They dissolve in organic solvents.
- (e) R—X (except R—F) burns with a green flame when interacted with Cu wire. (Beliestein test)
- (f) Dipole moment order-

(i)
$$CH_3Cl > CH_3F > CH_3Br > CH_3I$$
 (ii) $Cl > Cl > Cl$

3.3 Chemical Properties

3.3.1 Nucleophilic substitution reaction (S_N):





(g) Reaction with KCN and AgCN:

$$\stackrel{\delta^{+}}{R} - \stackrel{\delta^{-}}{X} + \stackrel{\bigoplus}{KCN} \stackrel{\ominus}{-} \stackrel{Alc.}{-} \longrightarrow R - C = N + R - NC + KX$$

$$\stackrel{lonic}{lonic} \qquad cyanide \qquad lsocyanide$$

$$(major) \qquad (minor)$$

• :ČN ion is an ambident nucleophile.

(h) Reaction with KNO₂ and AgNO₂:

$$\stackrel{\delta^{+}}{R} \stackrel{\delta^{-}}{=} \stackrel{V}{X} + \stackrel{\bigoplus}{KO} \stackrel{\Theta}{=} NO \xrightarrow{\quad Alc. \quad} R \stackrel{}{=} O \stackrel{}{=} N = O + R \stackrel{}{=} NO_{2} + KX$$
 Ionic
$$\stackrel{Alkyl \ nitrite \quad Nitro \ alkane \quad (Major) \quad (Minor)}$$

(i) Reaction with NaOR' (Sodium alkoxide):

$$R$$
— X + $NaOR'$ — — — R — OR' + NaX

(williamson synthesis reaction)

(j) Reaction with NH₃:

$$R-X+NH_{3} \xrightarrow{\Delta} R-NH_{2} \xrightarrow{R-X} R-NH-R \xrightarrow{R-X} R-N-R$$

$$\downarrow R$$

$$\downarrow R-X$$

$$\downarrow R-X$$

$$\downarrow R-X$$

$$\downarrow R-X$$

$$\downarrow R-X$$

$$\downarrow R-X$$

$$\downarrow R$$

$$\downarrow R-X$$

$$\downarrow R$$

$$\downarrow$$

(k) Reaction with CH≡CNa:

$$R-X + CH \equiv CNa \xrightarrow{\Delta} R-C \equiv CH + NaX$$

If
$$CH_3 - C - X + CH \equiv \overline{C} \overset{+}{N} a \xrightarrow{\Delta} CH_3 - C = CH_2 + NaX + CH \equiv CH$$

 $CH_3 - C = CH_2 + NaX + CH \equiv CH$
 $CH_3 - C = CH_2 + NaX + CH \equiv CH$
 $CH_3 - C = CH_2 + NaX + CH \equiv CH$
 $CH_3 - C = CH_2 + NaX + CH \equiv CH$

3.3.2 Dehydrohalogenation : Alkyl halides undergo β - elimination on treatment with KOH (alc.) or NaNH₂.

$$R - \overset{\beta}{C}H_2 - \overset{\alpha}{C}H_2 - X + KOH(alc.) \xrightarrow{\Delta} R - CH = CH_2 + HX$$

$$CH_3 - CH_2 - CH_2 - CH_2 - Br + KOH(alc.) \xrightarrow{\Delta} CH_3 - CH_2 - CH = CH_2 + HBr$$



$$\begin{array}{c} \begin{array}{c} \begin{array}{c} H & Br \\ -+---+- \end{array} \\ CH_3-CH-CH-CH_3 & \xrightarrow{Alc.KOH} \end{array} \\ CH_3-CH-CH-CH_3 & \xrightarrow{Alc.KOH} \end{array} \\ \begin{array}{c} CH_3-CH-CH_3+CH_3-CH_2-CH-CH_2+HBr \end{array} \\ \\ But-2 \text{ -ene (80\%)} \\ \end{array}$$

3.3.3 Wurtz Reaction: $2RX + 2Na \xrightarrow{Dry ether} R - R + 2NaX$

When a mixture of different alkyl halides, $(R_1 - X)$ and $(R_2 - X)$ is used a mixture of alkane is formed -

$$R_1$$
—X + 2Na + X— R_2 — Dry ether Δ \longrightarrow R_1 — R_2 + R_1 — R_1 + R_2 — R_2 + NaX

3.3.4 Formation of Organometallic compounds:

- (i) $R X + Mg \xrightarrow{dry ether} RMgX$ (Grignard reagent)
- (ii) $2C_2H_5Br + 2Zn \xrightarrow{dry ether} (C_2H_5)_2 Zn$ (Frankland reagent) + $ZnBr_2$
- (iii) $4C_2H_5Cl + 4Na/Pb \longrightarrow (C_2H_5)_4Pb + 4NaCl + 3Pb$

Sodium lead Alloy Tetra ethyl lead (used as antiknocking agent)

3.3.5 Friedel - Crafts reaction:

4.0 DIHALIDES

General formula $C_nH_{2n}X_2$. Two H - atom of alkanes, replaced by two halogen atoms to form dihalides. Dihalides are classified as:

(a) **Gem dihalide**: The term Gem is derived from geminal means - same position.

Two similar halogen atoms are attached to same C - atom

- **(b) Vic dihalides :** Vic term from Vicinal means adjacent C atoms

Two halogen atoms are attached on adjacent carbon atom.

Ethylene dihalide Propylene dihalide

(1,2-Dihaloethane) (1,2-Dihalopropane)

(c) α , ω dihalides: Halogen atoms are attached with terminal C - atom. They are separated by 3 or more C - atoms. They are also known as polymethylene halides.

$$\begin{array}{cccc} \textbf{Ex.} & \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 & & & \text{(1,4-Dihalobutane)} \\ & \text{I} & & \text{I} & & \text{Tetramethylene dihalide} \end{array}$$



4

4.1 **General Methods of Preparation**

(a) Gem dihalides:

By the reaction of PCl₅ on carbonyl compound.

$$CH_{3} - C - H + PCl_{5} \longrightarrow CH_{3} - C - H + POCl_{3}$$

$$CI$$

$$CH_{3} - C - H + POCl_{5}$$

Acetaldehyde

Ethylidene chloride

Acetone

2, 2 - Dichloropropane

(ii) By addition of halogen acids on alkynes:

$$CH \equiv CH + HBr \longrightarrow CH_2 = CHBr \xrightarrow{HBr} CH_3 CHBr_2$$

Vinul bromide 1, 1 - Dibromoethane

(b) Vic-dihalides:

(i) By the addition of halogens to alkenes:

$$\begin{array}{c} CH_2 \\ \parallel \\ CH_2 \end{array} + Br_2 \longrightarrow \begin{array}{c} CH_2Br \\ \parallel \\ CH_2Br \end{array}$$

$$1,\ 2 \text{ - Dibromoethane}$$

$$CH_3-CH=CH_2+Br_2 \longrightarrow CH_3-CH-CH_2$$

$$Br Br$$

1. 2 - Dibromo propane

(ii) By the action of PCl_5 on glycols :

$$\begin{array}{ccc} \mathsf{CH_2OH} & & & \mathsf{CH_2Cl} \\ \mathsf{I} & & \mathsf{+2PCl_5} & \longrightarrow & \mathsf{I} \\ \mathsf{CH_2OH} & & \mathsf{CH_2Cl} \end{array} \\ + 2\mathsf{POCl_3} + 2\mathsf{HCl} \\ \end{array}$$

Physical Properties 4.2

- Lower members are colourless, oily liquids with sweet smell. Higher members are solid.
- These are heavier than water.

4.3 **Chemical Properties**

(i) Action of KOH(alc.): (Dehydrohalogenation)

$$\begin{array}{cccc} CH_2X & & CH_3 & & CH\\ \begin{matrix} I & \\ CH_2X & & CHX_2 \end{matrix} & \xrightarrow{-2HX} & CH \\ \end{array}$$



(ii) Action of KOH(aq.): (Hydrolysis) It is a distinction test for gem - and vic - dihalides.

(a)
$$\begin{array}{ccc} CH_2-CI \\ CH_2-CI \\ CH_2-CI \end{array}$$
 + 2KOH(aq.) \longrightarrow $\begin{array}{ccc} CH_2-OH \\ CH_2-OH \\ \end{array}$ + 2KCl

Glyco

Vic-dihalide.

1, 2 - Ethanediol

(b)
$$CH_3CHXCH_2X$$
 $\xrightarrow{KOH(aq.)}$ $CH_3-CH-CH_2$ \downarrow \downarrow \downarrow OH OH Propane - 1, 2 - diol

$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CHX}_2 \end{array} \xrightarrow{\text{KOH }_{(\text{aq.})}} \begin{array}{c} \text{CH}_3 \\ | \\ \text{CHO} \end{array} \text{ and } \text{CH}_3\text{CX}_2\text{CH}_3 \xrightarrow{\text{KOH}(\text{aq.})} \text{CH}_3\text{COCH}_3 \end{array} \tag{Ketone}$$

Gem-dihalides

(iii) Reaction with KCN:

$$\begin{array}{c} \text{CH}_2\text{Cl} \\ \mid \\ \text{CH}_2\text{Cl} \\ + 2\text{KCN} \end{array} \xrightarrow{-2\text{KCl}} \xrightarrow{-2\text{KCl}} \xrightarrow{\text{CH}_2 - \text{CN}} \xrightarrow{\text{H}_2\text{O}/\text{H}^+} \xrightarrow{\text{CH}_2 - \text{COOH}} \xrightarrow{\Delta} \xrightarrow{\Delta} \xrightarrow{\text{CH}_2 - \text{CO}} \xrightarrow{\text{CH}_2 - \text{CO}$$

$$CH_{3}-CH < \begin{matrix} Cl & _{2KCN} \\ Cl & ^{-2KCl} \end{matrix} \rightarrow CH_{3}-CH < \begin{matrix} CN & _{H_{2}O/H^{+}} \\ CN & \end{matrix} \rightarrow CH_{3}-CH < \begin{matrix} COOH & _{\Delta} \\ COOH & \end{matrix} \rightarrow CH_{3}-CH_{2}COOH \end{matrix}$$
 Propanoic acid

- (i) CN group on acid hydrolysis gives COOH
- (ii) Two COOH group on one C atom always loose CO2 to form monocarboxylic acid on heating.
- (iii) Two COOH group on vic. C atom loose H₂O to form cyclic anhydride on heating.

(iv) Dehalogenation:

Vic.
$$CH_2Br \atop CH_2Br + Zn \xrightarrow{CH_3OH} CH_2 \atop CH_2Br + ZnBr_2$$

Same Carbon Product

BEGINNER'S BOX-1

- 1. Which of the following is not organometallic compound
 - (1) RMgX
- $(2) R_{o}Zn$
- (3) RONa
- (4) R₂Hg

- **2.** Which is Finkelstein reaction?
 - (1) $R-X + NaI \xrightarrow{acetone}$

(2) $R-X + AgF \longrightarrow$

(3) $R-X + NaF \longrightarrow$

 $(4) R-F + AgCl \longrightarrow$



5.0 TRI HALIDES (Haloform CHX₃)

- **General Method of Preparation** 5.1
 - From CH₄: $CH_4 + 3Cl_2 \xrightarrow{hv} CHCl_3 + 3HCl_3$
 - (ii) By Haloform reaction (lab method):

$$\begin{array}{c} \text{CH}_3\text{CH}_2 - \text{OH} \\ \text{or} \\ \text{CH}_3\text{COCH}_3 \end{array} \begin{array}{c} \text{Bleaching powder } [\text{CaOCl}_2] \\ \text{H}_2\text{O}/\Delta \end{array} \\ \text{CHCl}_3 \end{array} \begin{array}{c} \text{(HCOO)}_2\text{Ca} \\ \text{(CH}_3\text{COO)}_2\text{Ca} \end{array}$$

Mechanism:

$$\begin{split} \text{CaOCl}_2 \ + \ \text{H}_2\text{O} &\longrightarrow 2\text{Cl} \ + \ \text{Ca} \ (\text{OH})_2 \\ \text{CH}_3\text{CH}_2\text{-OH} \ + \ 2\text{Cl} &\longrightarrow \text{CH}_3\text{CHO} \ + \ 2\text{HCl} \\ \text{CH}_3\text{CHO} \ + \ 6\text{Cl} &\longrightarrow \text{CCl}_3\text{CHO} \ + \ 3\text{HCl} \\ \text{CCl}_3\text{CHO} \ + \ \text{Ca} \ (\text{OH})_2 &\longrightarrow \text{CHCl}_3 \ + \ (\text{HCOO})_2\text{Ca} \\ \end{split}$$

If CH₂COCH₃ is used then CHCl₃ is formed into 2 steps (Chlorination and Hydrolysis)

(+) ve haloform reaction: Reaction which gives haloform with alkali and X_2 is called as (+) ve haloform reaction.

Aldehydes: Only acetaldehyde CH 3—C—H

Ketones:
$$CH_3 - C - Z$$

Ex . CH
$$_3$$
 — C — CH $_3$, CH $_3$ — C — CH $_2$ — CH $_3$, CH $_3$ — C — CH $_2$ CH $_3$ etc. (All methyl ketones) O

CH
$$_3-C-COOH$$
 , CH $_3-C-CHO$ Also show haloform reaction. $\begin{bmatrix} & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ \end{bmatrix}$

(-) ve haloform reaction: Reaction in which haloforms are not formed with X_2 and alkali.



(iii) Preparation of pure CHCl₃:

$$\text{CCl}_3\text{CHO. 2H}_2\text{O} \xrightarrow{\text{NaOH}} \text{CHCl}_3 + \text{HCOONa} + 2\text{H}_2\text{O}$$

Chloral hydrate (Pure Chloroform)

Chloral can also be used in preparation of D.D.T.

$$CCl_3CH = O + 2H - O - Cl \xrightarrow{H_2SO_4} CCl_3CH - O - Cl$$

Dichloro diphenyl trichloro ethane (DDT)

(iv) Industrial preparation:

5.2 Physical Properties

CHCl₃ is colourless and sweet smelling liquid. It's B.P. is 61° C and it is insoluble in H₂O and have density more than H₂O. Chloroform is used as Anaesthetic.

5.3 Chemical Properties

(i) Oxidation:
$$CHCl_3 + [O] \xrightarrow{Air and light} COCl_2 + HCl$$

Phosgene gas or

Carbonyl Chloride

(Poisonous gas)

 $\mathrm{CHCl_3}$ is stored in dark coloured bottles which are filled upto the brim to prevent oxidation of $\mathrm{CHCl_3}$ into $\mathrm{COCl_2}$ and 1% ethanol is also added to chloroform

$$O = C < Cl \\ Cl \\ + 2HO - C_2H_5 \xrightarrow{-2HCl} O = C < OC_2H_5 \\ OC_2H_5$$

[Poisonous]

Diethyl carbonate [Non-Poisonous]

GOLDEN KEY POINTS

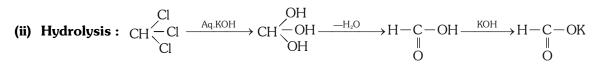
Test of CHCl₃

Reagent Pure CHCl₃ Impure CHCl₃ (COCl₂ +HCl)

Blue litmus No Change turns into red

AgNO₃ No reaction White ppt of AgCl

Conc. H₂SO₄ No reaction Yellow solution



Unstable



(iii) Carbyl amine reaction or isocyanide test: (Hoffman's carbylamine reaction)

Primary–Amines (Aliphatic or Aromatic) $\xrightarrow{\text{CHCl}_3 + \text{KOH}}$ Isocyanides Isocyanides have unpleasant or offensive smell (Isocyanide test).

$$R-NH_2 \xrightarrow{CHCl_3+KOH} R-NC$$

Mechanism:

$$\begin{array}{c} \text{CHCl}_{3} \xrightarrow{\text{KOH}} : \text{CCl}_{2} \\ & \text{(electrophile)} \end{array}$$

$$R = NH_{2} + : \text{CCl}_{2} \longrightarrow R = N = C$$

$$R = N$$

$$R$$

(iv) Reimer Tieman's reaction:

$$\begin{array}{c} \text{OH} \\ & \xrightarrow{\text{CHCl}_3 + \text{KOH}} \end{array} \\ & \xrightarrow{\text{Salicylaldehyde (o-Hydroxy benzaldehyde)}}$$

Mechanism : $:CCl_2$ is neutral attacking electrophile (formed by $\alpha, \alpha-$ elimination reaction)

Note: If CCl₄ is used in place of chloroform, salicylic acid is formed as product.

$$\begin{array}{c}
OH \\
& (i) (CCl_4 + KOH), \Delta \\
& (ii)H^{\oplus}
\end{array}$$

$$\begin{array}{c}
OH \\
COOH \\
(Salicyclic acid)$$



(v) Reaction with CH₃COCH₃:

$$CH_3 - C - CH_3 + H - CCl_3 \xrightarrow{\bullet OH} CH_3 - C - CH_3$$

$$OH CCl_3$$

Chloritone (Hypnotic)

(vi) Reaction with HNO_3 :

$$CCl_3 - H + HO - NO_2 \longrightarrow CCl_3 - NO_2 + H_2O$$

Chloropicrin or nitrochloroform

(Tear gas)

(vii) Reaction with CH₃CH=CH₂:

$$CH_{3}-CH=CH_{2}\xrightarrow{CHCl_{3}/Peroxide} CH_{3}-CH-CH_{2}$$

$$| | | | | | | CCl_{3}$$

$$| H CCl_{3}$$

A free radical addition reaction

(viii) Reaction with Ag : $CHCl_3 \xrightarrow{Ag} CH \equiv CH$

(ix) FCR: $3Ph - H + CHCl_3 \xrightarrow{AlCl_3} Ph_3CH$ Triphenyl methane

GOLDEN KEY POINTS

Iodoform Test

$$\begin{array}{c|c} CH_3CH_2OH & & & & & \\ or & & & & \\ CH_3COCH_3 & & & \\ \end{array} \xrightarrow{I_2+ \text{ NaOH or NaOI or OI}} & \rightarrow & CHI_3 \\ & & & & \text{yellow crystals} \\ & & & \text{of iod of orm} \\ \end{array}$$

• CHI₃ give yellow ppt. of AgI with AgNO₃ but CHCl₃ does not give AgCl ppt.

Reason: CHI3 is thermally less stable than CHCl3.

lodoform test can be used to distinguish the following pairs of compounds.

- (i) CH₃CH₂OH and CH₃OH
- (ii) CH₃CHO and CH₃CH₂CHO
- (iii) 2-Pentanol and 3-Pentanol
- (iv) Acetophenone and benzophenone
- (v) 2-Propanol and 1-Propanol

Freons

The chlorofluoro derivatives of methane and ethane are called freons.

CF₂Cl₂ – (dichloro difluoro methane)

C₂F₂Cl₄ – (Tetrachloro difluoroethane)

Most useful is CF₂Cl₂ (Freon-12)



Nomenclature of freons:

Freon – cba

$$c = n_{c-1}$$

 $b = n_{H+1}$
 $a = n_{E}$

$$c = n_{C-1} = 1 - 1 = 0$$

$$c = n_{C-1} = 1 - 1 = 0$$

$$c = n_{C-1} = 2 - 1 = 1$$

$$c = n_{C-1} = 2 - 1 = 1$$

$$b = n_{H+1} = 0 + 1 = 1$$

$$a = n_F = 2$$

$$c = n_{C-1} = 2 - 1 = 1$$

$$b = n_{H+1} = 0 + 1 = 1$$

$$a = n_F = 4$$
Freon-114

• Excess use of Freons is harmful for Ozone layer (depletion of Ozone layer).

6.0 Grignard Reagent

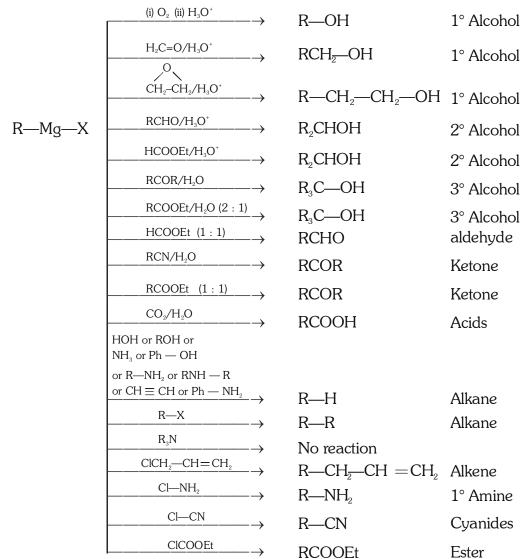
6.1 General Method of Preparation

Grignard reagents are prepared in the laboratory by the action of alkyl halides on magnesium metal in the presence of dry ether.

$$R-X+Mg$$
 \xrightarrow{dry} R — Mg — X (Grignard reagent) (Alkyl magensium halide)

The ease of formation of Grignard reagent is in the order RI > RBr > RCl Ether is used to dissolve the Grignard reagent by coordination.

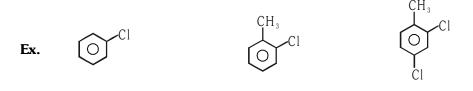
6.2 Chemical Reactions





7.0 Haloarene

If halogen atom is directly attached to the benzene ring, then compound is called as Haloarene.



(Chlorobenzene)

(2-Chlorotoluene)

(2,4-Dichlorotoluene)

7.1 General Methods of Preparation

(1)
$$\bigcirc$$
 + Cl_2 $\xrightarrow{AlCl_3}$ \bigcirc + HCl

(2)
$$OH$$

$$+ PCl_5 \xrightarrow{\Delta} OH$$

$$+ PCl_5 \xrightarrow{\Delta} + POCl_3 + HCl$$

$$3C_6H_5OH + POCl_3 \longrightarrow (C_6H_5)_3 PO_4 + 3HCl$$

7.2 Chemical Properties

(1)
$$OH$$

$$+ NaOH \xrightarrow{\text{(i) } 623K, 300 atm} OH$$

$$+ NaCl$$

Presence of electron withdrawing group on ring makes the nucleophilic substitution easier.

Reactivity Order: (Towards nucleophilic substatitution)

(2) Fittig reaction:

(3) Wurtz fittig reaction:



(4) Electrophilic Substitution Reaction:

Note: Cl is o- and p-directing group.

(ii)
$$\bigcirc$$
 + HNO₃ $\xrightarrow{\text{conc. H}_2\text{SO}_4}$ \bigcirc \bigcirc + \bigcirc NO₂ + \bigcirc NO₂

(Major)

(Major)

(iv)
$$\bigcirc$$
 + CH₃Cl $\xrightarrow{anhy. AlCl_3}$ \bigcirc Cl CH_3 + \bigcirc CH $\xrightarrow{CH_3}$ (Major)

BEGINNER'S BOX-2

- **1.** Which can give haloform with X_2/OH^- ?
 - (1) CH₃OH

(2) CH_3 - CH_2 -CH=O

(3) CH₃CHO

- (4) CH₃CH₂CH₂OH
- 2. Which of the following compounds cannot be identified by carbylamine test?
 - (1) $C_6H_5-NH-C_6H_5$

(2) CH₃CH₂NH₂

(3) CHCl₃

- (4) $C_6H_5-NH_2$
- 3. For preparation of Grignard reagent from haloalkanes which metal is used :-
 - (1) Na

(2) Mg

(3) Ca

(4) Ag

ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2					
DLOMNLK 3 DOX-1	Ans.	3	1					
BEGINNER'S BOX-2	Que.	1	2	3				
BEGINNER 3 BOX-2	Ans.	3	1	2				



EXERCISE-I (Conceptual Questions)

GENERAL METHOD OF PREPARATION

- 1. Alkyl halides can be obtained by all methods excepts
 - (1) CH_3 — CH_2 —OH + HCl $ZnCl_2$
 - (2) $CH_2 = CH CH_3 + HBr \longrightarrow$
 - $(3) C_0H_EOH + NaCl \longrightarrow$
 - (4) $CH_3COOAg + Br_9 / CCl_4 \xrightarrow{hv}$
- 2. Which of the following will not give iodoform test

- (2) $C_2H_5-C-C_2H_5$
- (3) H—CH₂—CH—C₂H₅ OH
- (4) I—CH₂—C—CH₂—H
- **3.** Which of the following product is obtained when bleaching powder is distilled with acetone
 - (1) CCl₄
- (2) CHCl₃
- $(3) CH_3 CH_3$
- (4) All
- **4.** Which will give yellow ppt. with iodine and alkali
 - (1) Propan-2-ol
- (2) Benzophenone
- (3) Methyl acetate
- (4) Acetamide

PHYSICAL PROPERTIES

- **5.** Which of the following has the highest boiling point
 - $(1) CH_3CH_2I$
- (2) CH₂Cl
- (3) CH₃I
- (4) CH₂Br
- **6.** A compound containing two –OH groups attached with one carbon atoms is unstable but which one of the following is stable
 - (1) CH₃CH OH
- (2) CH₃—C—OH OH
- (3) Cl₃C-CH(OH
- (4) All

CHEMICAL PROPERTIES

- 7. Arrange the following compounds in decreasing order of reactivity in SN^1 reaction:-
 - (a) Ph-CH₂-Cl

(c) Cl

- (1) a > c > b > a
- (2) c > d > b > a
- (3) a > b > c > d
- (4) b > a > c > d
- 8. $OH \xrightarrow{CHCl_3+KOH} Product.$

about above reaction the incorrect statement is

- (1) The name of reaction is Reimer-Teiman's reaction
- (2) The intermediate in the reaction is dichloro carbene
- (3) The final product is salicylaldehyde
- (4) The final product is benzyl chloride
- **9.** The purity of CHCl₃ can be checked by
 - (1) treating CHCl₂ by NaOH
 - (2) treating CHCl₃ by HCl
 - (3) treating CHCl₂ with aq. AgNO₃
 - (4) treating CHCl₃ by C_9H_5 -OH
- **10.** Pure CHCl₃ and pure CHI₃ can be distinguished by
 - (1) treating with litmus paper
 - (2) treating with aq. KOH
 - (3) treating with HCl
 - (4) treating with aq. AgNO₃
- 11. Arrange the following compound in decreasing order of reactivity in SN^2 reaction.
 - (a) CH_3 -C- CH_2 -Br
 - (b) CH₃-CH₂-CH₂-CH₂Br
 - (c) CH₃-CH-CH₂-Br
 - (d) CH₃-CH-CH₂CH₃
 - (1) b > c > d > a
- (2) a > b > c > d
- (2) b > c > a > d
- (4) c > a > b > d

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Shrivastava Classes, D-27, Near JVTS Garden, Chattarpur Extension New Delhi - 110074 **12.** Which of the following undergoes hydrolysis most easily

(3)
$$NO_2$$
 NO_2 NO_2

$$(4) NO_{2} CI NO_{3}$$

- 13. Which of the following is used as insecticide
 - (1) D.D.T.
- (2) Chloritone
- (3) CHCl₃
- (4) All of them
- **14.** Which of the following when heated with KOH and primary amine gives carbylamine test
 - (1) CHCl₃
- (2) CH₂Cl₂
- (3) CH₃OH
- (4) CCl₄
- **15.** Which reaction gives elimination as a major product

$$(1) CH_3-C-ONa + CH_3-Br \longrightarrow CH_3$$

(2)
$$CH_3$$
- CH_2 - $Br + NaCN \xrightarrow{DMSO}$

(3)
$$CH_3$$
- CH_2 -Br + NaI $\xrightarrow{Dry acetone}$

(4)
$$CH_3$$
 \downarrow
 CH_3
 $C-Br + CH_3ONa \longrightarrow CH_3$

- **16.** Iodoform gives a precipitate with ${\rm AgNO_3}$ on heating but chloroform does not because
 - (1) Iodoform is ionic
 - (2) Chloroform is covalent
 - (3) C-I bond in iodoform is weak and C-CI bond in chloroform is strong
 - (4) None of the above

17. Which reaction product is wrong (major) product.

(1)
$$CH_3CH_2CHCH_3 \xrightarrow{\bigodot OH/\Delta} CH_3CH_2CH=CH_2$$

(2)
$$CH_3CH_2CHCH_3 \xrightarrow{\Theta \oplus ONa} CH_3CH_2CH=CH_2$$
Br

$$(4) \bigcirc Br \xrightarrow{CH_3ONa} \bigcirc$$

- **18**. When alkyl magnesium halide reacts with $R-NH_{2}$, the product is
 - (1) R R
- (2) R—H
- (3) R₂NH
- (4) R-X
- **19.** Chloroform on reaction with acetone gives:-
 - (1) Acetylene
- (2) Chloretone
- (3) Nitrochloroform
- (4) Chloroacetone
- **20.** Chloroform reacts with aniline and aqueous KOH gives:-
 - (1) $Ph N \stackrel{?}{=} C$ (Phenyl isocyanide)
 - (2) Benzene
 - (3) Phenyl cyanide
 - (4) None of these
- 21. Which reaction product is wrong (major) product

$$(1) \bigcirc Br \xrightarrow{Zn(dust)} Dr$$

(2)
$$CH_3CH_2CH_2Br \xrightarrow{Nal} CH_3CH_2CH_2I$$

(3)
$$CH_3CHCHCH_3 \xrightarrow{Zn(dust)} CH_3CH=CHCH_3$$
Br Br

(4)
$$CH_3CH_2CHCl_2 \xrightarrow{\text{(i)NaNH}_2\text{(excess)}} CH_3C \equiv CH$$

- **22.** Which of the following undergoes nucleophilic substitution by SN^1 mechanism at fastest rate :
 - (1) CH₃-CH₂-Cl
- (2) CH₃-CH-Cl
- (3) $\langle O \rangle$ -CH₂-Cl
- (4) (O)-Cl



23. Which of the following pair is differentiated by iodoform test?

(4)
$$CH_2$$
, CH_2

24. Identify z in the following series

$$CH_2 \!\!=\!\! CH_2 \!\! \xrightarrow{\quad HBr \quad \quad \Delta} \!\! x \!\! \xrightarrow{\quad Hydrolysis \quad \quad } \!\! y \!\! \xrightarrow{I_2 \, / \, NaOH} z$$

- (1) C_2H_5I
- (2) C_oH_eOF
- (3) CHI₃
- (4) CH₃CHO

25.
$$I_2 \rightarrow A + B \rightarrow C \rightarrow D$$

Identify D:-

26. $C_6H_5CCl_3 \xrightarrow{Cl_2} X$

In the above reaction X is

(4) None of these

Rate of reaction is maximum if G is :-

- (1) -OCH₃
- $(2) CH_3$
- (3) –NO₂
- (4) -H
- **28.** Which does not gives iodoform test:

(2)
$$Ph$$
- C - CH_3

EXERCISE-I (Conceptual Questions) ANSWER KE											KEY				
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	2	2	1	1	3	4	4	3	4	2	4	1	1	4
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28		
Ans.	3	3	2	2	1	1	3	2	3	2	1	3	4		

EXERCISE-II (Assertion & Reason)

Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

- (A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.
- **(B)** If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.
- **(C)** If Assertion is True but the Reason is False.
- **(D)** If both Assertion & Reason are false.
- Assertion: Alkyl halides are not soluble in water.
 Reason: Alkyl halide does not form H-bonds with water molecule although alkyl halide is polar in nautre.
 - (1) A
- (2) B
- (3) C
- (4) D
- Assertion: CHCl₃ is more acidic than CHF₃.
 Reason: Electronegativity of Fluorine is more than chlorine.
 - (1) A
- (2) B
- (3) C
- (4) D
- Assertion: Isobutanal does not give iodoform test.

Reason: It does not have α -hydrogen.

- (1) A
- (2) B
- (3) C
- (4) D
- **4**. **Assertion**:—Styrene on reaction with HBr gives 1-bromo-1-phenylethane.

Reason:—Benzyl radical is more stable than alkyl radical.

- (1) A
- (2) B
- (3) C
- (4) D

5. **Assertion**: Rate of alkaline hydrolysis of methyl chloride to methanol is higher in DMF than in water.

Reason: Hydrolysis of methyl chloride follows second order kinetics.

- (1) A
- (2) B
- (3) C
- (4) D
- **6. Assertion** :- 2-Bromo butane on reaction with alcoholic KOH mainly gives 2-butene.

Reason: The hydrogen on C_3 carbon is more acidic than hydrogen on C_1 carbon.

- (1) A
- (2) B
- (3) C
- (4) D
- **7. Assertion**: Chlorobenzene is less reactive than benzene for electrophilic substitution reaction.

Reason: Resonance effect in chlorobenzene destabilized carbocation intermediate.

- (1) A
- (2) B
- (3) C
- (4) D

EXERCISE-II (Assertion & Reason)

ANSWER KEY

Que.	1	2	3	4	5	6	7
Ans.	1	2	3	2	1	3	3

